



# Graphitic Carbon Nitride Stabilized Water-in-Water Emulsions

Jianrui Zhang, Bradley D. Frank, Baris Kumru, and Bernhard V. K. J. Schmidt\*

**Aqueous multiphase systems have attracted a lot of interest recently especially due to target applications in the biomedical field, cosmetics, and food. In turn, water-in-water Pickering emulsions are investigated frequently. In here, graphitic carbon nitride (g-CN) stabilized water-in-water Pickering emulsions are fabricated via the dextran and poly(ethylene glycol)-based aqueous two-phase system. Five different derivatives of g-CN as the Pickering stabilizer are described and the effect of g-CN concentration on droplet sizes is investigated. Stable emulsions (up to 16 weeks) are obtained that can be broken on purpose via various approaches, including dilution, surfactant addition, and most notably light irradiation. The novel approach of water-in-water emulsion stabilization via g-CN opens up considerable advances in aqueous multiphase systems and may also introduce photocatalytic properties.**

Aqueous two-phase systems (ATPS) gained increased attention recently, which is not only due to new applications in polymer science, synthetic biology or biology but also for the larger goal of sustainable chemical processes that can be performed in completely water-based environments.<sup>[1,2]</sup> In addition, ATPS allow for advanced applications in cosmetics, food, biotechnology and drug delivery where more toxic components should be avoided.<sup>[1,3]</sup> As such, considerable effort is put in replacing oil-in-water emulsions by completely water-based water-in-water (W/W) emulsions. ATPS can be dispersed by a variety of methods and will reliably relax to a two-phase system unless diluted to the point where the polymers are dilute enough to become miscible.

To stabilize the mixed phases and thus form W/W emulsions, a Pickering emulsion approach is the key.<sup>[4,5]</sup> The requirement

of solid particle (Pickering) stabilizers is due to the fact that the interface in ATPS is rather wide in the range of tens of nanometers and can be overcome by larger entities only.<sup>[6]</sup> In addition, ATPS feature ultralow interfacial tensions in the range of  $\mu\text{N m}^{-1}$ .<sup>[7]</sup> Although the interfacial tension between two aqueous polymer solutions is significantly smaller than between oil and water, solid particles can adhere to the interface to inhibit coalescence of droplets, leading to efficient stabilization. Therefore, particles located between two aqueous phases are incapable of leaving spontaneously. A common example for an ATPS is poly(ethylene glycol) (PEG) and dextran in water, which has been applied for W/W emulsion formation frequently. A

variety of Pickering stabilizers have been reported, for example liposomes,<sup>[8]</sup> poly(lactic acid)-based platelets,<sup>[9]</sup> poly(dopamine) particles,<sup>[10]</sup> silica particles<sup>[11]</sup> or clay particles.<sup>[12]</sup> An example of particular interest is the spontaneous adsorption of protein microgels at the W/W interface that led to very efficiently stabilized water compartments.<sup>[13]</sup> Recently, we could show temperature-sensitive W/W emulsion stabilization utilizing thermal induced aggregation of a double hydrophilic block copolymer.<sup>[14]</sup>

Graphitic carbon nitride (g-CN) is a polymeric material, composed of repeating tri-s-triazine units and has gained broad attention as a metal-free photocatalyst in the visible range recently.<sup>[15]</sup> In addition to its metal-free nature, it is produced at a relatively low cost and in a tunable approach allowing for a large variety of uses.<sup>[16,17]</sup> In the past years, g-CN found use in a variety of applications including photo degradation for waste-water treatment,<sup>[18]</sup> CO<sub>2</sub> reduction,<sup>[19]</sup> water splitting,<sup>[20]</sup> in combination with polymers,<sup>[21,22]</sup> polymerization catalyst<sup>[23]</sup> and the production of hydrogels.<sup>[24]</sup> Due to its relevant application portfolio, new uses for g-CN are highly sought after, also to find new combinations of applications. For example, g-CN has been introduced as Pickering stabilizer for oil-in-water emulsions recently.<sup>[25,26]</sup>

In here, W/W emulsions are described utilizing g-CN as Pickering stabilizers and studied via optical microscopy as well as confocal laser scanning microscopy (CLSM) (**Scheme 1**). Various g-CN derivatives are introduced with different surface chemistry and the effect of g-CN concentration on emulsion formation studied. Finally, demulsification via surfactant addition, dilution and light irradiation is described.

Water/organic Pickering emulsification stabilized via g-CN was reported before and largely benefits from their nanosheet shape (Figure S1, Supporting Information).<sup>[25,26]</sup> Analogously due to g-CN nanosheet structure, it acts as a stabilizer in W/W

J. Zhang, B. D. Frank, Dr. B. Kumru, Dr. B. V. K. J. Schmidt  
Max Planck Institute of Colloids and Interfaces  
Am Mühlenberg 1, Potsdam 14476, Germany

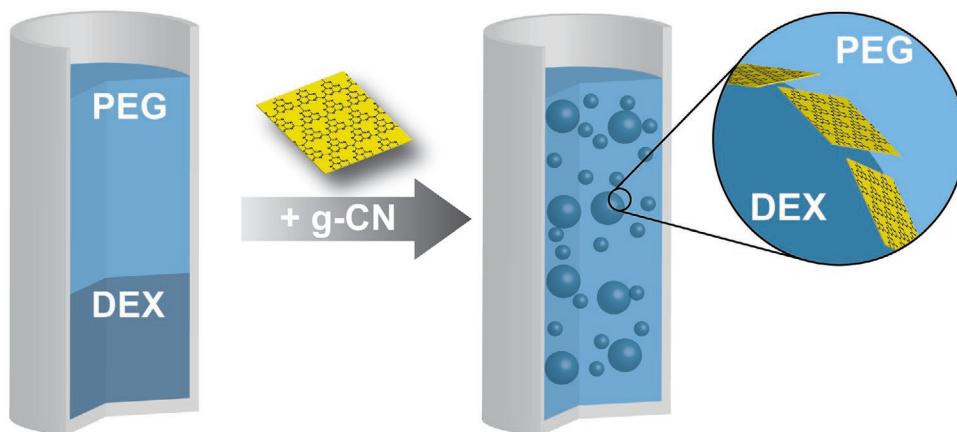
Dr. B. V. K. J. Schmidt  
School of Chemistry  
University of Glasgow  
Glasgow G12 8QQ, UK  
E-mail: bernhard.schmidt@glasgow.ac.uk

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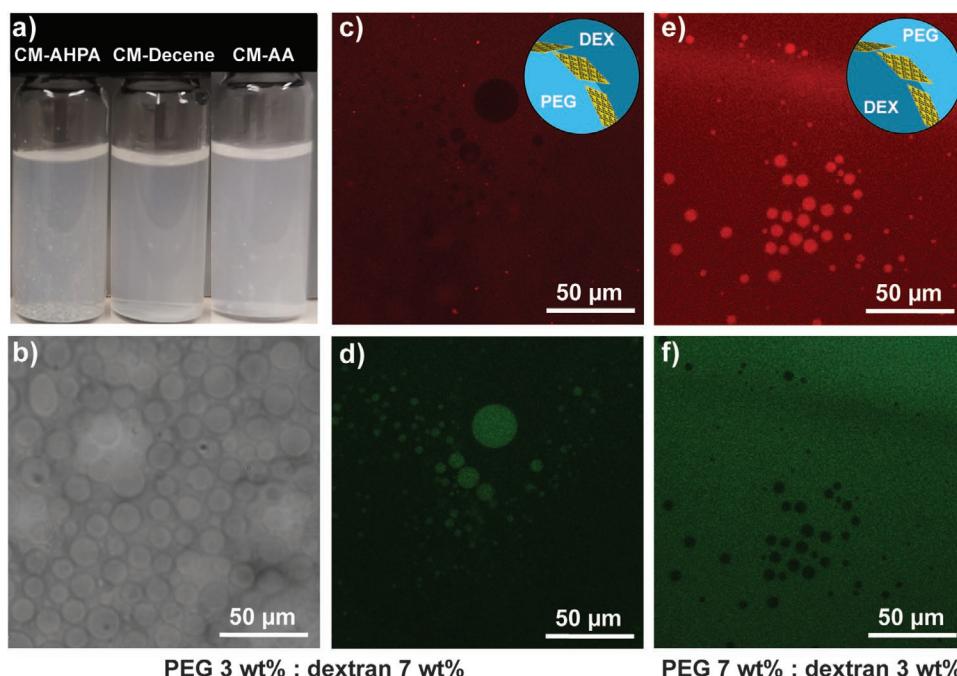


**Scheme 1.** Formation of W/W Pickering emulsions via g-CN stabilization (PEG: poly(ethylene glycol); DEX: dextran).

emulsions as well. Thus, W/W emulsions were successfully produced with the common PEG/dextran ATPS employing a variety of g-CN variants with different functionalities, e.g., g-CN from cyanuric acid-melamine complex (CM),<sup>[27]</sup> allylamine-grafted CM (CM-AA),<sup>[28]</sup> 3-allyloxy-2-hydroxy-1-propanesulfonic acid-grafted CM (CM-AHPA),<sup>[28]</sup> decene-grafted CM (CM-Decene),<sup>[28]</sup> and 4-methyl-5-vinyl thiazole-grafted phenyl-modified CM (CMP-TA).<sup>[29,30]</sup> All these g-CN variants used for emulsion preparation were effective stabilizers for the ATPS 3 wt% PEG<sub>35K</sub>: 7 wt% dextran<sub>40K</sub>, which can be verified via optical microscope showing emulsion droplets and macroscopic inspection (Figure 1, and Figures S2 and S3, Supporting

Information). Interestingly, W/W emulsions could be formed with a broad range of functional g-CN showing that g-CN is a versatile Pickering stabilizer. In addition, all emulsions could be formed at a quite low g-CN concentration (0.01 g L<sup>-1</sup>), although the droplets showed a rather broad size distribution.

CM-AHPA was utilized in the following studies due to its high dispersibility in water. Furthermore, DLS of CM-AHPA indicated an average hydrodynamic diameter of 232 nm, which is in the right range to be a successful Pickering emulsion stabilizer for W/W emulsion.<sup>[31]</sup> A considerable point in the successful formation of g-CN stabilized W/W emulsions is the preparation method. Homogenization was used throughout the



**Figure 1.** Graphitic carbon nitride stabilized Pickering emulsions (30 s homogenizer 22000 RPM): a) photographs of example emulsions; b) optical microscopy images of 0.02 g L<sup>-1</sup> CM-AHPA stabilized emulsion from 3 wt% PEG<sub>35K</sub>: 7 wt% dextran<sub>40K</sub>; c,d) confocal image from 3 wt% PEG<sub>35K</sub>: 7 wt% dextran<sub>40K</sub> emulsion droplets stabilized with 0.02 g L<sup>-1</sup> CM-AHPA displaying PEG (stained with FITC) in the droplet phase and dextran (stained with RhB) in the continuous phase as well as e,f) confocal image from 7 wt% PEG<sub>35K</sub>: 3 wt% dextran<sub>40K</sub> emulsion droplets stabilized with 0.02 g L<sup>-1</sup> CM-AHPA displaying PEG (stained with FITC) in the continuous phase and dextran (stained with RhB) in the droplet phase.



studies as it provided the most evenly reproducible and long-term stable emulsions, although other methods like sonication and mixing overnight are viable as well (Figure S4, Supporting Information). Nevertheless, passive mixing before homogenization showed to be important in the formation of g-CN stabilized PEG: dextran W/W emulsions, as a proper settling of both phases in the g-CN dispersion allows for improved emulsion droplet formation. When allowed to mix and homogenize, the resulting emulsion is an even, continuous phase of emulsion which is stable for (at least) 16 weeks (see below).

Especially in the case of W/W emulsions an important question is the composition of droplet and continuous phase. The control of the droplet and continuous phase is necessary due to its relevance for applications. Therefore, CLSM experiments were performed in order to elucidate the polymer partition in the phases of the emulsion. Two ATPS and corresponding emulsions were formed with CM-AHPA, i.e., 3 wt% PEG<sub>35K</sub>: 7 wt% dextran<sub>40K</sub> emulsion as well as 7 wt% PEG<sub>35K</sub>: 3 wt% dextran<sub>40K</sub> emulsion. In order to visualize the phases, fluorescein labeled PEG (20k) and rhodamine labeled dextran (70k) were added. For 3 wt% PEG<sub>35K</sub>: 7 wt% dextran<sub>40K</sub>, PEG is contained within the emulsion droplets (Figure 1 and Figure S5, Supporting Information), while in the case of inverted weight ratio (7 wt% PEG<sub>35K</sub>: 3 wt% dextran<sub>40K</sub>) dextran was located within the emulsion droplets (Figure 1 and Figure S6, Supporting Information). Given the changing continuous and emulsion phase based on the weight ratio of PEG<sub>35K</sub>: dextran<sub>40K</sub> within the ATPS, the emulsion type varied in either dextran-in-PEG emulsion or PEG-in-dextran emulsion. CM-AHPA does not show any preference to either the dextran or the PEG phase, allowing for the phases of the emulsion to switch by the weight content of the ATPS-forming polymers. As such, the polymer phase inside the droplet can be controlled and changed on purpose (Figure 1).

As the particle size for the utilized g-CN nanosheets is below 300 nm, the employed g-CN can only be observed at the interface in the form of larger aggregates in CLSM. In order to visualize the interfacial activity of g-CN, more concentrated (0.1 g L<sup>-1</sup>) dispersions of g-CN and hand mixing were utilized, which yielded larger emulsion droplets for better confocal imaging as well as g-CN aggregates. These g-CN aggregates could be observed at the edge of the emulsion droplets alluding to the presence of adsorbed g-CN at the water–water interface (Figure S7, Supporting Information), which was not indicated for low concentrations of g-CN at 0.02 g L<sup>-1</sup> (Figure 1) due to low amount of g-CN aggregates and small emulsion droplet size. Thus, it can be concluded that g-CN is acting as the Pickering stabilizer for PEG-dextran W/W emulsion system.

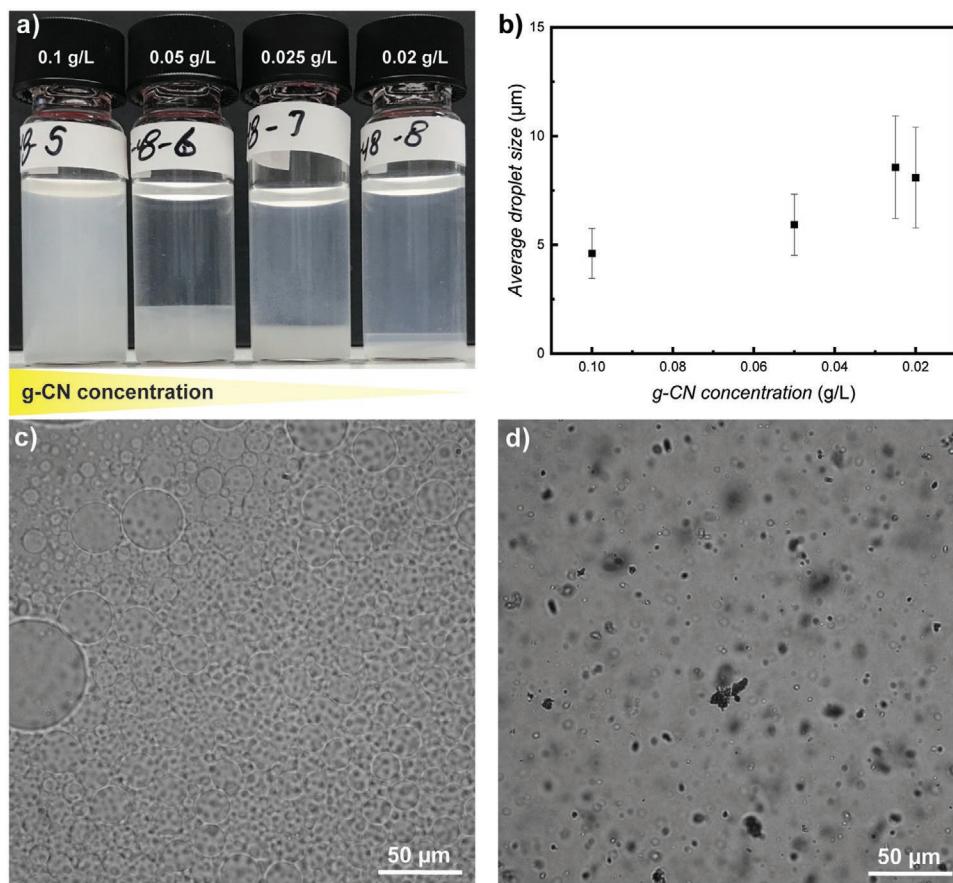
Notably, after emulsification the formation of two phases can be observed as well as a solid phase. The solid phase is due to an excess of g-CN that settles from the emulsion. Therefore, the formed phases and the effect g-CN concentration were investigated in more detail. For all samples investigated in the g-CN Pickering emulsion system, regardless of the g-CN concentration, if two phases appear in the sample, the top phase contains an emulsion with fewer g-CN aggregates than the bottom phase. The bottom phase contains almost no droplets and a large amount of g-CN aggregates as well as settled g-CN (Figure 2). The concentration of g-CN in the system has few effects on the emulsion formation itself as emulsions can be

successfully and stably made for a wide range of g-CN concentrations (0.1–0.001 g L<sup>-1</sup>; at 0.005 g L<sup>-1</sup> no more emulsion was observed, Figure S8, Supporting Information). Furthermore, g-CN concentration can be correlated to the distribution of each phase of the ATPS. For samples with a g-CN concentration decreasing from 0.1 to 0.01 g L<sup>-1</sup>, an emulsion can be formed with a decreased volume of nonemulsified phase. At the point of 0.02 g L<sup>-1</sup> almost the entire system consists of emulsified upper part (Figure 2a). The well-dispersed diluted g-CN dispersion changed the phase system, which reveals a one-phase emulsion with decreasing concentration of g-CN (Figure 2). This effect can be probably referred to a decreased aggregation tendency of diluted g-CN dispersions yielding effectively more surface-active stabilizer than concentrated g-CN dispersions.

In addition, the emulsion droplet size varies with the amount of g-CN in the dispersion as well. The observed droplet sizes show a weak correlation with g-CN concentration, i.e., with increasing g-CN concentration the average droplet size increase in a range from 4.6 to 8.6 μm (Figure 2b and Figure S9, Supporting Information) for the droplet system obtained via homogenization. The negative correlation between droplet size and g-CN concentration is mainly due to the aggregation of g-CN in water. The higher the concentration of g-CN in dispersion, the more easily g-CN aggregates are formed in water. Consequently, the aggregation of g-CN contributed to decreasing emulsion droplet size as less amounts of active stabilizers are present. A different situation is observed in the case of emulsion preparation via shaking, which leads to larger droplets that decrease in size from 63.6 to 32.1 μm (Figure S10, Supporting Information) with increasing g-CN concentration. The difference to homogenization is probably due to the fact that shaking does not break g-CN aggregates in the first place. Nevertheless, for both emulsion preparation methods the distribution of droplet sizes is quite broad, making accurate sampling of the emulsion challenging, albeit, the general trend of the emulsion droplet size is sustained.

Next, the long-term stability of g-CN stabilized W/W emulsions was studied. The stability of the emulsions was examined by monitoring the droplet sizes against aging time in ambient environment. Stability was assessed for both high-concentrated of 0.1 g L<sup>-1</sup> (Figure S11, Supporting Information), medium concentrated of 0.05 g L<sup>-1</sup> (Figure S12, Supporting Information) and lower concentrated g-CN dispersions 0.02 g L<sup>-1</sup> (Figure S13, Supporting Information). Droplet size varies over the entirety of the sample, however, the largest portion of droplets are very small. Samples showed no significant change in emulsion droplet size and were stable over the course of 16 weeks. The stability of the emulsion droplets was not affected by g-CN concentration, i.e., CM-AHPA-based emulsions were stable for at least 16 weeks at various concentrations.

Demulsification studies were conducted in order to test the stability of Pickering W/W emulsions under several conditions, including dilution of the system, the addition of a surfactant (SDS) and light irradiation. For all cases, the emulsions could be broken on purpose. Emulsion stability toward surfactants was tested with the addition of 4 × 10<sup>-3</sup> M sodium dodecyl sulfate (SDS) and observed with optical microscopy (Figure S14, Supporting Information). The introduction of negatively charged SDS has a profound effect on g-CN stabilization. The



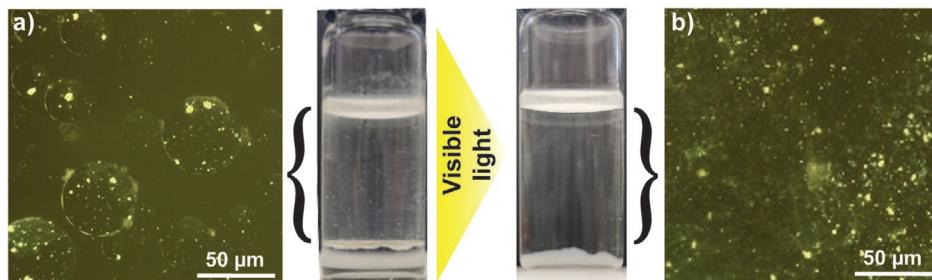
**Figure 2.** Effects of g-CN concentration on W/W 3 wt% PEG<sub>35k</sub>: 7 wt% dextran<sub>40K</sub> emulsions (30 s homogenizer 22000 RPM): a) The macroscopic change in phases as the concentration of g-CN decreases (0.1, 0.05, 0.025, 0.02 g L<sup>-1</sup>), b) average droplet sizes for different CM-AHPA concentrations, c) optical microscopy of the upper phase of a CM-AHPA W/W emulsion (0.02 g L<sup>-1</sup> CM-AHPA in 3 wt% PEG<sub>35k</sub>: 7 wt% dextran<sub>40K</sub> emulsion), and d) the corresponding lower phase of a CM-AHPA W/W emulsion.

hydrophobic part of surfactant interacts with the g-CN surface, which leads to electrostatic repulsion between individual g-CNs and thus droplet coalescence is initiated as the solid-stabilizer is expelled from the droplet surface.

Demulsification via dilution was tested by addition of water equal to half the system size (50%), equal to the system size (100%), and twice the system size (200%) (Figure S15, Supporting Information), which was imaged via optical microscopy. As expected, dilution is very effective at breaking these ATPS emulsions because the system ends up below the binodal and forms a single phase. In choosing to work near the critical point

for phase formation, we were able to use a minimal amount of polymer to achieve ATPS, and allow more room for viscosity changes. Emulsions with higher water dilution (200%) broke quicker than those with a lower dilution (50%) as expected. The emulsion may withstand a certain amount of dilution but as the two phases become miscible the emulsion will eventually break into a continuous solution.

As g-CN is well-known for its photoactivity, the effect of visible irradiation in CM-AHPA stabilized W/W emulsions was investigated. Therefore, the emulsions were irradiated with a visible light LED for 24 h (Figure 3). Macroscopically no considerable



**Figure 3.** CM-AHPA (0.05 g L<sup>-1</sup>) stabilized W/W 3 wt% PEG<sub>35k</sub>: 7 wt% dextran<sub>40K</sub> emulsions (30 s homogenizer 22000 RPM): a) emulsion phase before and b) after visible light irradiation for demulsification.



change was observed, yet optical microscopy revealed demulsification. Interestingly, light irradiation did not only demulsify the W/W emulsion but also break the ATPS itself as no two liquid phases were observed afterward. The bottom phase did contain no emulsion but rather solid particles (Figure S16, Supporting Information). In order to clarify the origin of the light induced demulsification, several control reactions were performed. At first, another Pickering stabilizer was investigated, namely poly(dopamine) particles (PDP),<sup>[10]</sup> which showed no sign of demulsification after visible light irradiation (Figure S17, Supporting Information). As expected, g-CN stabilization seems to be the reason for the light sensitivity. Next, it was investigated whether the surface functionality of CM-AHPA was the reason for the effect. Therefore, CM-stabilized emulsions were probed, which led to a similar result as with CM-AHPA (Figure S18, Supporting Information). It was noticed that the pH of the mixture shifted significantly from 7 to 2 after irradiation for the g-CN systems, in contrast to the PDP system. It can be assumed that the shift in pH leads to the demulsification, which was also observed via addition of HCl (Figure S19, Supporting Information). A reference experiment with CM in water did not show a change in pH, while irradiation of a dextran solution in water in the presence of CM revealed a decrease in pH. Therefore, the origin of the pH shift can be attributed to the photo oxidation of dextran, which leads to the formation of acidic byproducts.<sup>[32,33]</sup> The degradation of dextran could be observed via size exclusion chromatography (SEC) that showed a decrease in molar mass of the emulsion constituents with irradiation time (Figure S20, Supporting Information). Interestingly, a fast decrease of molar mass is observed at the beginning of the reaction, while only minor changes are observed in later stages of the reaction. In addition to the pH change the decrease in molar mass affects the stability of the two-phase system.<sup>[34]</sup>

In conclusion, a novel way of W/W emulsion stabilization based on g-CN and the PEG/dextran ATPS has been described in the present contribution. Various g-CN derivatives showed remarkable Pickering stabilization properties leading to stable emulsions up to 16 weeks as observed via optical microscopy and CLSM. Moreover, the concentration of g-CN could be used to tune the droplet size. Interestingly, the W/W emulsions could be demulsified on purpose via various approaches, including dilution, surfactant addition and most notably light irradiation. Especially, demulsification via light irradiation is an uncommon direction in W/W emulsions that will enable various opportunities for future applications. Overall, the novel approach of water-in-water emulsions stabilization via g-CN opens up significant developments in aqueous multiphase systems and might also introduce photocatalytic properties to these systems.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

aqueous two-phase systems, carbon nitride, responsive emulsions, water-in-water emulsions

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